

Cellulosic forms with a functional effect and a method for producing the same

The invention relates to cellulosic forms as well as a method for producing cellulosic forms by the dry-wet extrusion process with improved and enhanced functional effects, especially applicable in medicine, hygiene, garment, paper manufacturing and packaging industry.

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The functional effect is directed to a steady and meticulously adjustable bactericide effect, especially for wound contact material, sports and leisure clothing, hospital textiles, filter and packaging papers.

Prior art

It is well known that heavy metal ions like e.g. silver, quicksilver/mercury, copper, zinc and zirconium ions are deadening or growth inhibiting to bacteria, viruses, fungi or spores (Thurman et al., CRC Crit. Rev. In Environ. Contr. 18 (4), P. 295-315 (1989)).

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With respect to the bactericide effect silver ions are of particular interest. The important advantage of silver ions against other bactericide metal ions, like e.g.  $Hg^{2+}$ , is the insensibility of the human metabolism against silver. The bactericide acting concentration is denoted for silver as 0,01 – 1 mg/l (Ullman's Encyclopedia of Industrial Chemistry (5. Edition), VCH 1993, Volume A 24, P. 160).

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This effect of silver ions is used in different applications. In the manufacture of textile fibres silver is for example galvanically deposited on the surface of polyamide silk. Working up of said galvanically silver-plated polyamide silk on knitters and moulders is problematical, since the silver layer of the polyamide silk is partially deposited on the yarn leading devices leading to numerous shut downs of said devices. It is further known to introduce metallic silver, silver-zeolite or silver-glass ceramics into the matrix of the fibre of melt spun fibres like polypropylene fibres, polyester fibres and polyamide fibres (Taschenbuch für die Textilindustrie 2003, Schiele & Schön Berlin, P. 124 ff).

The use of silver-zeolite and silver-glass ceramics was also proposed for acrylic fibres. Also cellulosic fibres with bacteriostatic and bactericidal properties are available on the

market. Incorporation of triclosan (2,4,4-trichloro(II)-hydroxyphenyleneether) into cellulosic fibres leads to a permanently bacteriostatic fibre (ITB International Textile Bulletin 3/2002). Said substance is active against bacteria usually occurring on skin, including pathogenic staphylococcus-types.

DE 10 140 772 discloses a method for producing cellulosic forms with incorporated algae. Said forms are able to adsorb metals from heavy metal containing media. The heavy metal loaded forms may be used as antibacterial and/or fungicidal material. The content of adsorbed heavy metals in said cellulosic forms is given as at least about 70 mg/kg, related to the total weight of the cellulosic forms.

It is further disclosed that by dipping a fibre with a content of brown algae of 11,39 weight-%, based on the weight of the fibre, into a 0,05 M AgNO<sub>3</sub>-solution a silver content of 1855 mg/kg per fibre was obtained. Since algae are natural products the capacity for binding said heavy metals varies. During binding of heavy metals onto algae different binding mechanisms are relevant, like ion exchange, complexing and further unknown reactions. The binding of said heavy metals onto said algae is therefore non-specific. A further disadvantage of said fibre is that only cations may be used for a bactericidal effect, but no bactericidal anions, e.g. benzoic acid and sorbic acid.

WO 00/63470 relates to a method for the production of cellulosic forms with a high adsorption ability, wherein usual ion exchange particles with grain size of >=25µm are added to said forms prepared by the Lyocell method. Furthermore, the adsorption of heavy metal ions is disclosed, namely of copper and lead, with a capacity of 0,01 mmol/g, using an anion exchanger of a styrene-divinyl benzene copolymer.

Patent Abstracts of Japan, Edition 0152, No. 01 (C-0834) of JP 3 054234 discloses the production of a cellulosic composition comprising an ion exchanger functionality, useful as binder for metal ions, wherein said production process consists of mixing a specifically generated cellulose and an anionic polymer followed by solidification of said mixture.

#### Aim of the invention

Aim of the present invention is to provide a cellulosic form with functional effect as well as a method for preparing said cellulosic form, especially for the use in medicine, hygiene and garment, wherein said forms have a bactericide effect and wherein especially said advantages go along with breathable clothing. A further aim is to keep said active agents in a textile depot and further to obtain sufficient release of said agent should be controllable. Further the forms, especially fibres or foils, obtainable by the method of the invention, should be formed thus, that they are useful for preparing wound overlays, band-aids, sanitary products, textiles, special papers and packaging material, because of the high adsorption ability of active agents. Finally composites including differing fibres should be producible.

10 Further advantages are shown in the following description.

The aim is reached in combination with the aforementioned discussed method according to the present invention by charging the cellulosic forms, wherein said forms are spun according to the dry-wet extrusion method and having incorporated weakly linked cationic active ion exchangers with active agents. Surprisingly it was found that the binding capacity for said active agents depends on the degree of cross-linking of  
20 the ion exchanger. Thus, the binding capacity for the cationic active agents, like e.g. silver could be increased by more than the double amount, if polyacrylates are used, which were weakly cross-linked by a multifunctional cross-linker.

Weakly cross-linked ion exchangers according to the present invention are ion exchangers with a decreased amount of cross-linkers. Usual ion exchanger resins show an amount of cross-linkers of 4 to 12 weight-%, based on the weight of the ion exchanger resin. Weakly cross-linked ion exchangers according to the present invention have an amount of cross-linkers ranging from 0,1 to 2,0 weight-%, preferably 0,3 to 1,5 weight-%, particularly preferably 0,5 to 1,2 weight-%.

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Weakly cross-linked ion exchanger resins are characterized by the pronounced ability to swell considerably in aqueous solutions. Usual ion exchange resins with the aforementioned amount of cross-linkers show only a minor degree of swelling.

Fibres made with incorporated weakly cross-linked cation exchangers show a capacity for binding silver ions which surpasses the capacity of fibres with brown algae according to DE 10 140 772 up to the 28-fold. Thus, the opportunity is given to produce fibres or foils which may be heavily loaded with cationic active bactericide agents like silver ions. A fibre with 15 weight-% incorporated weakly cross-linked cationic ion exchanger may be loaded with about 80 g silver. Silver loads of fibres of >100 g Ag/kg fibre are possible, if the amount of the incorporated weakly cross-linked cation exchanger is increased accordingly.

- 10 Said fibres may be mixed with other fibres, e.g. cotton, wool or synthetic fibres, to produce yarns with the desired silver content. This procedure allows the production of bactericidic yarns in a very economic way.

However, incorporation of ion exchangers leads with an increasing amount within the fibre to a disadvantageous influence on the textile physical parameters like strength, elongation and loop strength. In particular strength and loop strength will be reduced with an increasing amount of incorporated ion exchanger.

- 20 Thus, it is also of economic interest to provide silver loaded fibres showing textile physical properties, like strength and loop strength which come close to the properties of fibres which do not contain incorporated ion exchangers.

- With the present invention it is possible to obtain fibres with a sufficient content of silver per fibre to show an adequate bactericide effect, but no disadvantages in view of the textile physical parameters. According to the present invention it is possible with 0,5 to 1,5 weight-%, based on the cellulose weight of the fibres, of incorporated weakly cross-linked cation exchanger to bind 5000 to 10.000 mg Ag/kg fibre. Such fibres have a sufficient bactericide effect in the known field of use and are equal to non-modified fibres concerning their textile physical parameters. Processing of such fibres and yarns made thereof is possible on all kind of textile machinery.

If, instead of weakly cross-linked cation exchangers, ion exchangers are used on the basis of acrylic acid-divinylbenzene-copolymer-bound carboxyl groups or on the basis of a styrene-divinylbenzene-copolymer bound chelat forming imino-diacetic-acid as described in DE 19 917 614, fibres are obtained, which are comparable in their

bactericide effect. However, the capacity for silver ions is less than 50 % of the aforementioned weakly cross-linked cation exchangers.

A measure for the bactericide effect of the fibres or yarns is the equilibration concentration of the active agent in aqueous solutions e.g. the concentration of the silver ions.

For this purpose fibres or yarns loaded with silver ions are put into distilled water at a temperature of 20° C, followed by a measurement of the equilibration concentration of

10 the silver ions after 24 h. Table 1 shows the equilibration concentrations of silver ions and the load of silver in the fibres, while using weakly cross-linked cation exchangers or known ion exchangers cross-linked with divinyl-benzene. As shown the equilibration concentration of silver ions is on a level which is above the necessary concentration of 0,01 to 1 mg/l to obtain a bactericide effect. The equilibration concentration may be controlled to each desired concentration level by mixing with other kinds of fibres.

Table 1

content of ion exchanger 7 weight%	Ag-content of the fiber [g/kg]	equilibration-concentration [mg/l Ag <sup>+</sup> ]
ion exchanger with -COOH-groups	13,5	2,9
ion exchanger with chelating groups	17,5	3,6
weakly linked cation exchanger (inventive)	36,5	2,7

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As shown in table 1, the fibres according to the present invention provide the equilibration concentration which is necessary to obtain an antimicrobial effect, at an increased Ag-content of the fibre at the same time. The advantages thereof are obvious.

During the use of the fibres free Ag-ions are permanently released, whereby the equilibration concentration is upheld by the Ag deposited in the fibre. Due to the improved storing properties of the inventive fibres the equilibration concentration may be upheld over an extended period of time.

If weakly cross-linked cation exchangers and strongly basic anion exchangers, based on styrene-divinylbenzene-copolymer with trialkylammonium-groups in chloride-form are incorporated into the fibre, said fibres may be loaded with cation-active and anion-active bactericide ions, like silver ions and benzoic acid or asorbic acid.

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Thus, it is possible to use silver ions together with anion active agents like e.g. benzoic acid and asorbic acid. Said substances are toxicologically unobjectionable as shown in several publications and therefore they are qualified for a direct use in foods (Wallhäußer, Sterilisation, Desinfektion, Konservierung, 4<sup>th</sup> edition, time 1988, P. 396). Processing of such fibres in paper manufacturing or foils made thereof provide antimicrobial packages for food.

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Further, the use of said functionalised fibres with cation active agents within medical applications is possible. Such fibres may bind agents, like nicotine. Said fibres may be manufactured into band-aids and used for transdermal, therapeutic systems.

Advantageously loading of said functional fibres may proceed by dipping the fibres into a solution of appropriate ions. Said dipping may be carried out continuously or in batch mode. When dipping in continuous mode it is preferred to load the cut fibre in a separate bath during subsequent treatment.

The invention and its properties will be illustrated more clearly by the following examples:

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#### Example 1

Powdery weakly cross-linked cation exchanger, based on a cross-linked copolymerisate of acrylic acid and sodium acrylate, having a grain size < 10 µm, is added to 12 weight-% cellulose solution in N-methylmorpholine-N-oxide monohydrate, in a weight proportion of 15 weight-%, based on the cellulose proportion. This spinning

solution was homogenised in a kneader and spun with a spinning nozzle with 480 holes and a spinning hole diameter of 80 µm at a temperature of about 90° C. The draw off speed was about 30 m/min. The multifile fibre was led through several washing baths to wash out the residual N-methylmorpholine-N-oxides. The fibres were skidded and loaded in 10 L of 0,1 M silver nitrate solution per kg fibre. After loading the fibres were skidded and washed to remove residual silver nitrate. Finally the fibres are dried at a temperature of about 80° C.

Table 2

yarn-count	dtex	0,7
yarn-count related tensile tear resistance (dry)	cN/tex	22,5
elongation (dry)	%	14,8
yarn-count-related tear resistance of interwoven loops	cN/tex	7,5
Silver content	g/kg fiber	80

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Table 2 shows the parameters of the fibres as well as the silver content per fibre. A highly loaded fibre offers the advantage, that by blending this fibre with other textile fibres, e. g. cotton, silver loaded yarns can be economically obtained. For a content of roughly 5000 mg Ag/kg yarn the silver-fiber constitutes only a sixteenth of the yarn.

In contrast to the galvanised polyamide-fibres thus produced yarns show a good processability on knitting machines or moulders.

#### Example 2

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Fibres are produced according to example 1 with a titre of 0,17 tex and a content of weakly cross-linked cation exchanger of 6 weight-%, based on the content of cellulose. These fibres are loaded with silver according to example 1. The fibre-parameters are given in table 3.

### Example 3

Fibres are made according to Example 1 with a titre of 0,5 tex and a content of weakly cross-linked cation exchanger of 0,5 weight-%, based on the cellulosic content. The loading with silver ions is carried out according to Example 1. The parameters of the fibres are shown in table 3. Further, in table 3 a fibre without weakly cross-linked cation exchanger is shown for comparison.

Table 3

		example 2	example 3	fiber without weakly linked cation exchanger
yarn-count	d tex	0,17	0,5	0,5
yarn-count related tensile tear resistance (dry)	cN/tex	35,8	37,6	38,1
elongation (dry)	%	13,0	11,4	11,8
yarn-count-related tear resistance of loops	cN/tex	8,2	9,1	9,5
silver content	g/kg fiber	36,6	4,6	-

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It is evident from examples 1 to 3, that the silver content on a fibre is adjustable over a wide range via the content of weakly cross-linked cation exchanger. Even with 0,5 weight-% a high silver content is obtainable. The influence of 0,5 weight-% of the weakly cross-linked cation exchanger on the textile parameters of the fibre is marginal.

### Example 4 (Comparative example)

To a cellulose slurry in 60 % aqueous N-methylmorpholine-N-oxide an aqueous suspension of weakly acid macro-porous cation exchanger, based on styrene-20 divinylbenzene-copolymer with chelating groups of iminodiacetic acid, is added in such a concentration, that the spinned fibres reach a content of 6 weight-%, based on the cellulosic content. After spinning said fibres are washed and loaded with silver ions according to Example 1. Table 4 shows the parameters of the fibres.

Table 4

		example 4	example 5
yarn-count	d tex	0,5	0,5
yarn-count related tensile tear resistance (dry)	cN/tex	31,2	30,9
elongation (dry)	%	14,2	13,5
yarn-count-related tear resistance of loops	cN/tex	9,1	8,5
silver content	g/kg fiber	17,5	13,6

#### Example 5 (Comparative example)

Working corresponding to Example 4 and adding to the slurry 6 weight-% of a weakly acid macroporous cation exchanger, based on cross-linked polyacrylate in its sodium-form, so that the spun fibre contains 6 weight-% ion exchanger based on the cellulose content, washing said fibre and loading it with silver ions according to Example 1, one obtains fibres with 13,6 g Ag/kg per fibre. Example 5 surprisingly shows that the ion exchanger on the basis of polyacrylate binds about half the amount of silver ions compared to the weakly cross-linked cation exchanger based on polyacrylates. The rise of the binding capacity of more than 100 % leads to technical and economical advantages in that on one hand small amounts of the weakly cross-linked cation exchanger in the fibre barely influence the textile physical parameters, while on the other hand, based on the high incorporation of silver ions, an economical production by blending with other fibres is possible.

#### Example 6

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Fibres with weakly cross-linked cation exchangers as well as common ion exchangers of the prior art, made according to Examples 1 to 5 are loaded with silver, copper (II) and zinc ions. The results are shown in Table 5.

Table 5

fiber incorporated with	metal content g/kg fiber		
	copper	silver	silver/zinc
20 weight-% ion exchanger according to example 4 (comparative example)	23,7	57,1	23,9/27,5
20 weight-% ion exchanger according to example 5 (comparative example)	11,5	41,7	36,4/24,5
15 weight-% weakly linked cation exchanger as in example 1 to 3	25,5	85,5	59,3/30,5

Fibres loaded with copper ions, silver ions or a combination of silver ions and zinc ions may be used as bactericide fibres.

#### Example 7

A suspension of weakly cross-linked cation exchanger based on a cross-linked copolymerisate of acrylic acid and sodium acrylate and a strong basic anion exchanger, based on a styrene-divinylbenzene-copolymer with trialkylammonium-groups in chloride form, in 85 % N-methylmorpholine-N-oxide is added in such an amount to a 11 weight-% cellulose solution in N-methylmorpholine-N-oxide-monohydrate, such that the spinning solution contains 11 weight-% cellulose, based on the cellulose content, 8 weight-% of the weakly cross-linked cation exchanger and 8 weight-% of said anion exchanger. After homogenisation the spinning solution is spun according to Example 1 with a titre of 0,5 tex. The fibres show a strength of 26,3 cN/tex, an elongation of 12,1 % and a yarn-count related tear-resistance of loops of 8,6 cN/tex.

The silver load is at 52,4 g silver/kg fibre and the load with benzoate at 16,6 g benzoate/kg fibre. These fibres possess a very strong bactericide effect. The example shows the applicability of fibres according to the invention in combination with loaded fibres with anion exchangers and cation exchangers known from the prior art.

#### Example 8

Ion-exchanging fibres or foils according to the invention with incorporated cation exchangers, produced corresponding to example 2, are loaded with nicotine. The loaded fibres or foils are washed and dried. These fibres or foils can be processed into textile depots and can be applied as transdermal, therapeutic system.

#### Example 9

- 10 The bactericide properties of fibres, produced according to example 1, were determined following the European Pharmacopaeia (EP 2002), 'Bioburden determination'.

Papers were examined, which contain fibres according to example 1 in such an amount, that gradually altered silver contents in the paper of 190 mg Ag/kg paper, 760 mg Ag/kg paper and 3800 mg Ag/kg paper resulted. The examination was carried out with the following micro-organisms (Tables 6 – 9):

	Pseudomonas aeruginosa	ATCC 9027
20	Staphylococcus aureus	ATCC 6538
	Bacillus subtilis spores	ATCC 6633
	Fusarium solani spores	ATCC 36031.

Table 6 – Pseudomonas aeruginosa

silver content	microbial count after respective incubation time			
	0 minutes	1 day	3 days	7 days
comparative sample	$6.9 \times 10^4$	$7.8 \times 10^4$	$5.9 \times 10^5$	$4.5 \times 10^4$
190 mg Ag/kg	$8.9 \times 10^4$	$4.5 \times 10^3$	77	< 10
760 mg Ag/kg	$7.7 \times 10^4$	$1.3 \times 10^3$	< 10	< 10
3800 mg Ag/kg	$8.7 \times 10^4$	$3.3 \times 10^2$	< 10	< 10

Table 7 Staphylococcus aureus

silver content	microbial count after respective incubation time			
	0 minutes	1 day	3 days	7 days
comparative sample	$1.1 \times 10^5$	$1.2 \times 10^5$	$1.4 \times 10^5$	$9.6 \times 10^4$
190 mg Ag/kg	$1.3 \times 10^5$	$1.1 \times 10^5$	$4.6 \times 10^3$	36
760 mg Ag/kg	$1.4 \times 10^5$	$8.8 \times 10^4$	$4.8 \times 10^3$	< 10
3800 mg Ag/kg	$1.2 \times 10^5$	$4.9 \times 10^4$	$1.1 \times 10^3$	< 10

Table 8 Fusarium solani spores

silver content	microbial count after respective incubation time			
	0 minutes	1 day	3 days	7 days
comparative sample	$1.6 \times 10^5$	$1.7 \times 10^5$	$1.6 \times 10^5$	$1.7 \times 10^5$
190 mg Ag/kg	$1.6 \times 10^5$	$1.2 \times 10^5$	$1.0 \times 10^4$	< 10
760 mg Ag/kg	$1.2 \times 10^5$	$7.8 \times 10^4$	$7.3 \times 10^3$	< 10
3800 mg Ag/kg	$1.6 \times 10^5$	$8.8 \times 10^4$	$1.4 \times 10^3$	< 10

Table 9 Bacillus subtilis spores

silver content	microbial count after respective incubation time			
	0 minutes	1 day	3 days	7 days
comparative sample	$1.3 \times 10^5$	$1.2 \times 10^5$	$1.2 \times 10^5$	$1.3 \times 10^5$
190 mg Ag/kg	$1.1 \times 10^5$	$9.5 \times 10^4$	$9.7 \times 10^4$	$1.6 \times 10^4$
760 mg Ag/kg	$1.2 \times 10^5$	$1.1 \times 10^5$	$8.4 \times 10^4$	$1.7 \times 10^4$
3800 mg Ag/kg	$1.3 \times 10^5$	$8.8 \times 10^4$	$7.7 \times 10^4$	$1.1 \times 10^4$

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All results of the microbial count are afflicted with an error of measurement of 10%.

The comparative sample was a paper without silver-containing fibres. For all microorganisms a dependency of the microbicidal effect on duration of treatment and

concentration of the silver-load could be found. The bacillus subtilis spores showed the highest resistance as expected. But also with these micro-organisms a decrease in microbial count could be achieved.

#### Example 10

Fibres produced according to example 1 were spun in combination with cotton to stocking-yarn with a titre of Nm 68/1 and a silver content of 1300 mg Ag/kg yarn. With this yarn a hose was knitted and examined on its bactericide effect (sample 31444083).

- 10 The examination was carried out according to SN195924. The test-organism was lactobacillus brevis DSM 20054. As test sample a not anti-microbially equipped cotton fabric was used (Table 10). Five measurements were carried out on each sample as well as the test sample.

Table 10 – Results of the examination of the anti-bacterial effect in a germ carrying experiment with Lactobacillus brevis as examined germ

sample	lg KBE after X hours of contact					AE-values		rating
	0	0-average	2	6	24	AE6	AE24	
test 1	7,0	6,9	7,3	8,0	9,3	-1,1	-2,4	
test 2	6,8		7,2	8,0	9,3	-1,1	-2,4	
test 3	7,0		7,3	8,0	9,3	-1,1	-2,4	
test 4	7,0		7,0	8,0	9,4	-1,1	-2,5	
test 5	6,7		6,9	8,1	9,2	-1,2	-2,3	
3144408.1	6,9	6,9	6,2	3,0	4,2	3,9	2,7	+
3144408.2	6,9		6,4	3,5	6,1	3,4	0,8	+
3144408.3	6,9		6,2	4,5	4,0	2,9	2,9	+
3144408.4	7,0		6,2	3,0	6,2	3,0	0,7	+
3144408.5	7,0		6,1	3,5	6,2	3,4	0,7	+

20 KBE = number of colony-building units of test-bacteria

AE = antimicrobial effect

Evaluation-criteria:

The 24-hours-value of the growth-control (control, i. e. standard-fabric) has to be larger than the initial value by at least two orders of magnitude ( $AE < -2$ ).

An antimicrobial effect is given, if a KBE-value is at most 0,5 decadic logarithms above the average value of the KBE at zero contact time, i. e.  $AE_{5,24} > -0,5$ .

The effect of an antimicrobial equipment is given, if for the test-bacteria 4 of 5 single KBE-values of each contact time show an antimicrobial property. These requirements

10 are met by the results of sample number 3144408 (knitted hose).